Relation of Curie temperature and conductivity: (Ga,Mn)As alloy as a case study

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Abstract

Experimental investigations of diluted magnetic semiconductors indicate a strong relation between Curie temperature and conductivity. Both quantities depend non trivially on the concentration of magnetic impurities, the carrier density, and the presence of compensating defects. We calculate both Curie temperature and conductivity of (Ga,Mn)As alloys in a selfconsistent manner based on the same first principles Hamiltonian in which the presence of compensating defects is taken into account. The effect of As-antisites and Mn-interstitials is determined separately and a good agreement between theory and experiment exists only in the case where the dominating mechanism of is due to the Mn-interstitials.

The diluted magnetic semiconductors (DMS) represent a promising material for future applications in the spintronics as well as a system on which existing theories of finite-temperature magnetism and transport in complex diluted magnetic alloys can be critically tested. We refer the reader to a recent extensive review [1] of both theoretical and experimental efforts in this field. The best studied system up to now is (Ga,Mn)As for which reliable structural, magnetic, and transport data are now available. Samples with well defined structural and defect characterization are necessary requirement for any theoretical study, in particular that based on parameter-free approaches where quantitative agreement is one of the primary aims.

The Curie temperature (T_c) and the conductivity are among the most important characteristics of magnetic alloys and their parameter-free determination is thus of a great importance. Their internal relation was the subject of a recent experimental study [2]. A qualitative understanding of finite-temperature magnetism including an estimate of the Curie temperature [3] as well as of transport properties [4] can be obtained using the perturbative J_{pd}-model [1]. However, this approach fails quantitatively. Indeed, T_c is evaluated in the framework of the mean-field theory using the averaged lattice model [3] and thus explicitly neglecting the disorder in the system. The conductivity is calculated in the lowest order of the perturbation theory which underestimates the effects of the disorder.

In the present paper we wish to calculate T_c and the conductivity starting from the same, first principles Hamiltonian. This allows us to evaluate exchange integrals as well as transport properties on equal footings. A quantitative comparison of results of the parameter-free approach with corresponding experimental data will represent a crucial test of existing theories. First, the Curie temperature is determined beyond the average lattice approximation as concerns the effects of compensation and dilution and beyond the mean-field approach as concerns the effect of spin fluctuations [5, 6, 7]. Second, the conductivity is evaluated using the Kubo-Greenwood formula which represents a non-perturbative approach. We stress that the present approach has no adjustable parameters. Indeed, we will use for each sample the measured nominal Mn concentration and the carrier density which will be then used to estimate the concentration of compensating defects. We will consider, as compensating defects, separately As-antisites and Mn-interstitials and demonstrate a key relevance of the latter defects for a good quantitative agreement with experimental data [2].

We will now briefly describe methods used to calculate the Curie temperatures and con-

ductivities for samples at various states of annealing corresponding to a given nominal Mn-concentration.

We evaluate the Curie temperature in the spirit of a two-step model as suggested by Liechtenstein [8]. In the first step are total energies of low-lying magnetic excitations mapped onto the classical random Heisenberg model in which are the pair exchange integrals determined explicitly from energies corresponding to small rigid rotations of spins on the lattice in the framework of the adiabatic approximation by employing the Green function approach. In the second step, methods of statistical physics are used to estimate the Curie temperature for this Hamiltonian. This approach has proved to be very useful for a broad class of magnetic materials [9, 10], including the DMS [5, 6, 7]. We have implemented above approach in the framework of the all-electron scalar-relativistic tight-binding linear muffin-tin orbital (TB-LMTO) method in which the disorder due to various (small) defect concentrations is included in the framework of the coherent potential approximation (CPA) [11]. The CPA is known to reproduce reliably the compositional dependence of carrier concentrations as well as to describe correctly the transport relaxation time due to the presence of various defects in random systems. It should be noted that the same calculated carrier concentration and carrier lifetimes are used for the evaluation of exchange integrals and the conductivity in the present approach in a striking contrast to the J_{pd}-model where carrier lifetime is neglected and has to be implemented additionally for the evaluation of the conductivity. On the other hand, the CPA cannot describe properly behavior of electrons in localized states in which, for example, the hopping conductivity dominates. Here, however, we consider systems in the metallic regime.

The Curie temperature as determined from the Heisenberg Hamiltonian is due to transversal spin fluctuations neglecting thus the effect of longitudinal (Stoner) excitations. This is a good approximation for systems with large rigid magnetic moments such as Mn-impurities in GaAs semiconductor [9]. The main problem of reliable determination of T_c is the dilution, namely the fact that for low defect concentrations typical for DMS is the occurrence of long-range ferromagnetism strongly depending on the spatial extent of exchange integrals. This is particularly important for the present parameter-free approach in which exchange integrals are not fitted but their values and spatial extent are determined by underlying electronic structure. Recently, three groups have elaborated independently an approach in which random positions of impurities are incorporated in the framework of the Monte

Carlo sampling while corresponding transversal spin fluctuations are included either by the Monte Carlo approach [5, 6] or by using the selfconsistent local random-phase approximation (SC-LRPA) [7]. These theories have explained the reduction of T_c in diluted samples as compared to predictions based on the averaged lattice model neglecting disorder [12]. A detailed comparison with experiments for well annealed (Ga,Mn)As samples with very low concentrations of native defects (Mn-interstitials and As-antisites) has resulted in a good quantitative agreement between measured and calculated Curie temperatures (for the most detailed comparison see Ref. 7).

The next step in the quantitative comparison between the theory and experiment was the study, Ref. 13, in which it was demonstrated that Mn-interstitials rather than As-antisites are dominating defects reducing T_c as compared to optimally annealed samples. Such a model is supported by recent first-principles theoretical studies [14]. We will continue further and evaluate, for the same samples, corresponding conductivities and compare the resulting T_c vs conductivity relation with experiment [2].

The conductivity in (Ga,Mn)As is due to *p*-hole carriers which are through the *pd*-coupling scattered on defects present in the system, namely on Mn-impurities, Mn-interstitials, and As-antisites. Without external magnetic field, there are essentially three different contributions to the resistivity in (Ga,Mn)As alloys: (i) the scattering on phonons, acoustical eventually optical ones if they could be excited, (ii) the magnetic scattering due to thermodynamical fluctuations which is the largest at $T=T_c$ and which is essentially determined by the spin-spin correlation function [15], and (iii) the residual resistivity due to the presence of various defects.

The residual resistivity clearly dominates in the low temperature regime and in this paper we will limit ourselves to this case for which experimental data [2] are also available. Inclusion of the other above mentioned contributions is beyond the scope of the present paper. The linear-response theory (Kubo-Greenwood approach) [16] as formulated in the framework of the TB-LMTO-CPA approach is used to determine the residual conductivity of the sample. It should be noted that corresponding transport relaxation time is estimated in the framework of the same first-principles Hamiltonian as used for the estimate of exchange integrals. The theory formulated for the multi-sublattice case allows to include Mn-interstitials and As-antisites on equal footing with conventional Mn-impurities [17]. In addition, we have also implemented into the formalism disorder-induced vertex corrections

although their effect on the conductivity in the preaent case is relatively small (less than 10%). It should be noted that the present linear theory is unable to describe the hopping conductivity between states in well localized impurity subbands such as the Mn-impurity bands in Mn-doped GaN alloys. The conductivity is rather sensitive to various kinds of defects and therefore the sample preparation (the presence of defects) will play an important role for calculated values of the conductivity.

The Curie temperature of both as-grown and annealed samples of (Ga,Mn)As for a nominal concentration of Mn-atoms $x_{\rm Mn}$=0.067 was evaluated in Ref. 13. Here we briefly reiterate the main features of the theory. It was demonstrated that a small amount of As-antisites, e.g., 0.5%, will influence calculated T_c only negligibly (5-10 K). On the other hand, the dominant mechanism for compensation are Mn-interstitials and a good agreement between theory and experiment was obtained for both as-grown and annealed samples. Theory is based on the following simple model: Mn-interstitials are attracted by substitutional Mn-atoms on Ga-sublattice and form a singlet pair of spins with a strong antiferromagnetic coupling [14]. They have only weak influence on remaining magnetically active Mn-atoms with the effective concentration $x_{\rm eff}$=$x_{\rm Mn} - 2x^i_{\rm Mn}$, where $x_{\rm Mn}$ and $x^i_{\rm Mn}$ are, respectively, the nominal (total) concentration of Mn-atoms and the concentration of Mn-interstitials. We will thus eliminate these pairs from effective Heisenberg model for the determination of T_c. Further, by assuming that each Mn-interstitial adds two electrons (Mn-interstitial acts as a double donor), we obtain for the effective carrier concentration $n_{\rm eff}$ the relation $n_{\rm eff}$= $x_{\rm Mn} - 3x^i_{\rm Mn}$ [13]. In the framework of our model, we identify the experimental compensation ration, $\gamma_{\rm exp}$, with the effective compensation ratio $\gamma_{\rm eff}$=$n_{\rm eff}/x_{\rm eff}$. From known $\gamma_{\rm exp} = \gamma_{\rm eff}$ and the nominal Mn-concentration Mn we can determine $x_{\rm eff}$ and $n_{\rm eff}$ which are needed for the estimation of corresponding exchange integrals [10]. The first-principles theory, however, does not allow an independent variation of the concentration of active magnetic atoms and the carrier concentration. To overcome this problem one can adopt the rigid band model: a frozen electronic structure corresponding to $x_{\rm eff}$ is used and the Fermi energy is shifted so that required carrier concentration is obtained. This is, however, a non-selfconsistent procedure with obvious limitations. Instead, we have used effective doping by non-magnetic impurities which only negligibly influence states at the Fermi energy and thus also exchange integrals and thermodynamic magnetic properties. The doping is thus used as a purely computational device. In Ref. 13 we have used As-antisites as above described computational device. For-

mally, each singlet pair consisting of Mn-substitutional impurity on Ga-sublattice and the nearest-neighbor Mn-interstitial is thus replaced effectively by one half of the As_{Ga}-antisite. In this way are Mn-interstitals effectively excluded from the thermodynamical studies.

On the other hand, all defects contribute to the impurity scattering, and thus to the transport calculations, i.e., also magnetically inactive pairs of substitutional and interstitial Mn-impurities have to be included. It should be noted that the concentration of Mn-interstitial atoms can also be easily determined from known nominal Mn-concentration x_{Mn} and the compensation ratio γ. While a small concentration of As-antisites has negligible effect on values of T_c as already mentioned, their effect on transport properties has to be included. We have therefore performed three sets of transport calculations: (i) with As-antisites as the only compensating defect, (ii) assuming Mn-interstitials as compensating defects, and (iii) including additionally to Mn-interstitials also a small concentration of As-antisites. We have then compared theoretical results with experimental T_c vs conductivity data at low temperatures assuming that small concentration of As-antisites will not influence T_c as discussed above. In transport calculations we have assumed, in an agreement with theoretical calculations [14], antiparallel orientations of spin moments on substitutional and interstitial Mn-atoms in (Ga,Mn)As alloy and included disorder-induced vertex corrections.

The results are summarized in three figures, Fig. 1 for the model with As-antisites as compensating defect, Fig. 2 for a model with Mn-interstitials as compensating defects, and Fig. 3, where, in addition to Fig. 2, are also As-antisites included in transport calculations. The experimental data are for a nominal Mn-concentration $x_{Mn} = 0.067$ and various stages of annealing, ranging from as-grown sample (low T_c and conductivity) to an almost perfectly annealed sample (high T_c and conductivity). The theoretical data correspond to as-grown sample with $\gamma_{\rm eff}$=0.54, to partly annealed sample with $\gamma_{\rm eff}$=0.83, and to an almost perfectly annealed sample with $\gamma_{\rm eff}$=0.96. This corresponds, respectively, to $x^i_{\rm Mn}$=0.016, 0.009, and 0.0035. It should be noted that the effective carrier concentrations $n_{\rm eff}$ and/or corresponding compensation ratios γ are known with error-bar of order 15-20% [2, 18]. Above values of parameter γ are the same as those used in the paper [13]. In the model with both Mn-interstitials and As-antisites (Fig. 3), we have chosen the concentration of As-antisites $y_{\rm As}$=0.005 which is within the upper limit of uncertainty with which is known effective carrier concentration experimentally and which only negligibly (few K) influences the calculated Curie temperature. There are no experimental data in Ref. 2 concerning amount

of As-antisites but it is believed that some native As-defects are present even in well annealed samples. The experimental data used in Figs.1-3 correspond to the low-temperature measurements of the conductivity (T=4.2 K) but similar, almost linear dependence of T_c vs conductivity curve was obtained also for the room temperature [2], although here are conductivities reduced by phonons and by additional magnetic scattering due to thermodynamical fluctuations as described above.

The following conclusions can be made: (i) As-antisites as compensating defects fail to reproduce both the experimental T_c (see also [13]) and measured conductivity which seems to be too high in this model; (ii) the presence of Mn-interstitials significantly improves the quantitative agreement between theory and experiment by correctly reproducing an almost linear dependence of the Curie temperature on the conductivity with an acceptable quantitative agreement. While calculated T_c agree with experimental data very well (see also Ref. 13), the conductivity still seems to be slightly overestimated; (iii) the additional presence of a small amount of As-antisites not only reproduces the (almost) linear dependence of the Curie temperature on the conductivity but it also brings the theory into a good quantitative agreement with available experimental data.

We have presented a parameter-free theory which is able to reproduce simultaneously both the Curie temperature and the low-temperature conductivity measured in as-grown and annealed samples of (Ga,Mn)As. In addition, we have demonstrated that the inclusion of Mn interstitials into the theory is of crucial importance for a good quantitative agreement between theory and experiment. As-antisites are shown to play a secondary role.

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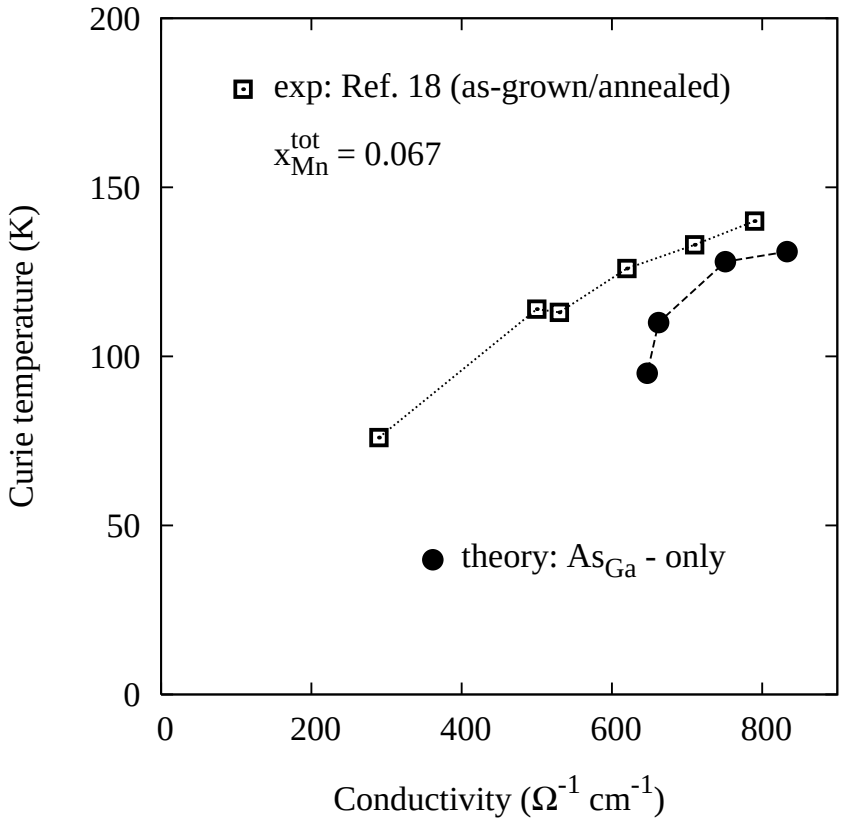

FIG. 1: T_c vs conductivity relation assuming that dominating compensating defects are As_{Ga}-antisites. Experimental results [18] for as-grown and annealed samples are also shown.

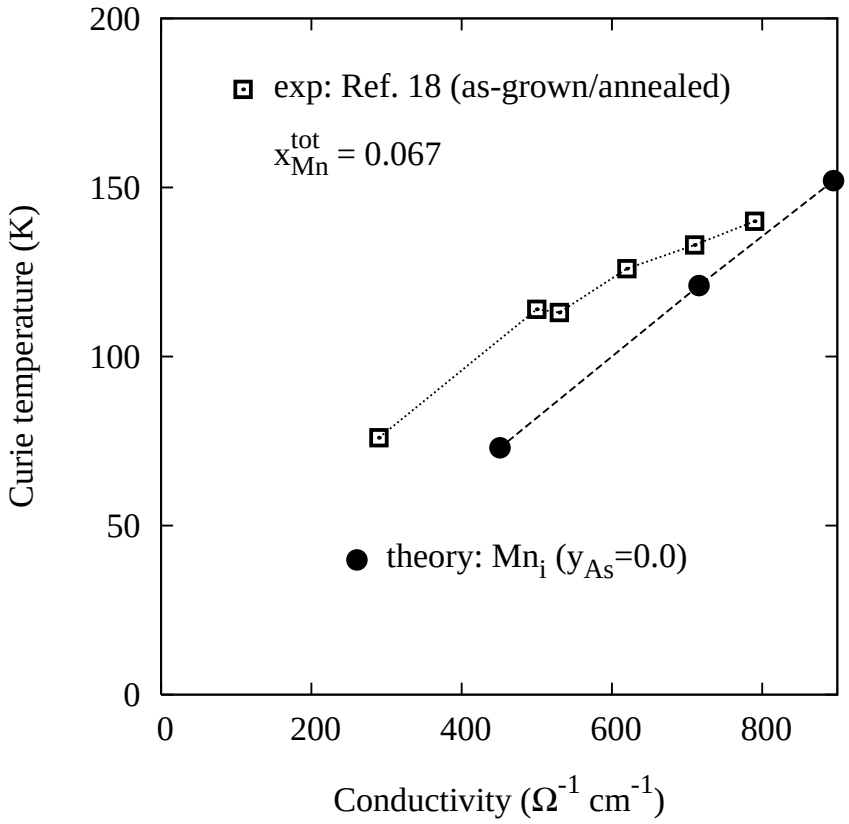

FIG. 2: T_c vs conductivity relation assuming that dominating compensating defects are Mn-interstitials. Experimental results [18] for as-grown and annealed samples are also shown.

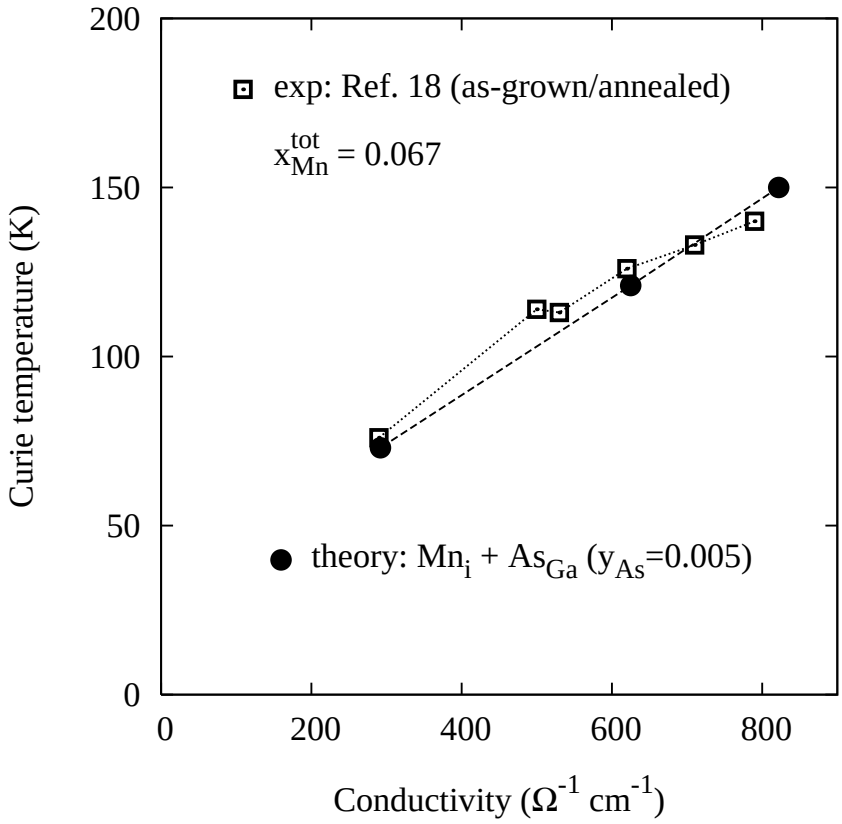

FIG. 3: T_c vs conductivity relation assuming that dominating compensating defects are Mn-interstitials but there is present also a certain concentration $y_{\mathrm{As}} = 0.005$ of $\mathrm{As_{Ga}}$-antisites. Experimental results [18] for as-grown and annealed samples are also shown.